

SPECIFIC VOLUME OF MINERAL-MATTER-FREE COKE

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ABSTRACT

A statistical method has been developed for obtaining the specific volume of mineral-matter-free coke without knowledge of the specific volume of the mineral matter contained therein, and the theoretical considerations on which it is based have been discussed. Specific volume-carbonizing temperature and composition-carbonizing temperature relations for mineral-matter-free cokes prepared from bituminous coals in the temperature range 500° to $1,000^{\circ}$ C. show that different reactions take place below and above 700° C. Specific volume-composition relations of crystalline aromatic hydrocarbons, mineral-matter-free cokes, and hypothetical aromatic hydrocarbons corresponding to the oxygen-, nitrogen-, and mineral-matter-free cokes are in accord with the view that a disordered crystalline structure exists in cokes from bituminous coals prepared in the carbonizing temperature range of 500° to $1,000^{\circ}$ C. An equation has been derived for calculating the specific volume of the hypothetical aromatic hydrocarbons.

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The establishment of the structure of an unknown substance through a study of its physical properties depends on prior knowledge of relations between physical properties and chemical structure of authentic compounds. Thus, density or its reciprocal, specific volume, an additive structural quantity, becomes one of the most important for such a purpose.

The constitutive nature of specific volume has been used recently to study the chemical structure of mineral-matter-free coal (1) (2). ^{1/} One of the difficulties involved in such a study concerns the mineral matter in coal, since even in specially prepared samples a small amount of mineral matter is unavoidable and chemical methods for its complete removal without modification of the coal substance are not available. Therefore, exact calculation of the specific volume of mineral-matter-free coal is possible only when the specific volume of the mineral matter is known.

There is no direct method for determining the mineral matter as such in coal. Data on the composition of coal ash are available, but to obtain the specific volume of the mineral matter from these data assumptions have to be made as to changes in the composition and density which took place during the ashing operation. An alternative is to assume that the specific volume of the ash is identical with that of the mineral matter. Such assumptions also involve the assumption that no organometallic combination exists in coal; in other words, that carbonaceous coal and mineral matter constitute a physical mixture.

Just as with coal, the specific volume of mineral-matter-free coke ^{2/} can be used for studying chemical structure. However, since the percentage of mineral matter is higher in coke than in its parent coal, the effect of specific volume of mineral matter upon the calculated specific volume of the mineral-matter-free coke will be greater.

The purpose of this paper is to present a statistical method to obtain the specific volume of mineral-matter-free coke in the absence of knowledge of the

^{1/} Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

^{2/} In this paper the term coke indicates both coke and semicoke from coking coals.

specific volume of the mineral matter, and to discuss relations of the specific volume of the mineral-matter-free coke and its composition with the temperature of preparation, and the significance of these relations to our knowledge of coke structure.

Relationship Between Carbonizing Temperature and Composition and Crystalline Structure of Coke or Char from Carbonaceous Materials

Statistical analysis of BM-AGA data ^{3/} has shown the dependence of the composition of cokes from bituminous coals upon carbonizing temperature (3) (4). Linear, semi-logarithmic relations have been shown to exist between the atomic hydrogen-carbon ratio and carbonizing temperature and the hydrogen content and carbonizing temperature, both expressed on a dry, ash-free basis. In the temperature range 500° to 1,100° C. these relations were expressed by the following equations: $\log H/C = 0.5616 - 0.001781 T$, and $\log H = 1.37 - 0.00165 T$, where H/C represents the atomic hydrogen-carbon ratio; H , percent hydrogen; T , carbonizing temperature in °C.

According to the same analysis (3) (4), both the average percent oxygen and the logarithm of the average percent volatile matter vary linearly with the carbonizing temperature. In the range 500° to 600° C. both the volatile matter and the oxygen contents of the parent coal were found to affect the respective content of the resulting coke significantly.

Furthermore, it has been shown that gaseous products from the carbonization of such widely different materials as glycine, bakelite, cellulose, bituminous coal, anthracite, and petroleum coke are similar in composition, particularly at temperatures above that of initial decomposition (5) (6). Chemical reactions during carbonization of coal, lignin, cellulose, and a number of organic compounds at constant heating rate (7) as well as those during degradation of cellulose and wood at constant temperatures (8) have been observed to be of first order.

It might, therefore, be expected that the mechanism of carbonization follows a general pattern for all carbonaceous materials, and that the relationships between the composition of the solid product and the carbonizing temperature, found by Lowry for cokes from bituminous coals (3) (4), would also be applicable to cokes or chars from carbonaceous materials of widely different composition.

Available data on atomic hydrogen-carbon ratios and hydrogen contents of cokes and chars from a wide variety of carbonaceous materials are plotted as functions of carbonizing temperature in Figures 1 and 2. The parent carbonaceous materials, data for which are plotted on the y-axis, include cellulose (9), coals of different ranks (9) (10), petrographic components (9), coal-tar pitch and its fractions (9) (11), and organic compounds (9) (11). The heating rate in each case was 5° C. per minute except when otherwise stated in the figure. The solid line in each figure represents Lowry's equation for cokes from bituminous coals.

^{3/} Data from Bureau of Mines survey on carbonizing properties of American coals, using Bureau of Mines-American Gas Association method.

These plots show that during heating the slopes of the H/C vs. T and % H vs. T lines for any carbonaceous material change sharply at a temperature which may be defined as the decomposition point of the material, and then generally follow the slopes corresponding to the appropriate Lowry equation. The decomposition temperature of the carbonaceous material decreases with an increase of the atomic hydrogen-carbon ratio or the hydrogen content of the material. From the same plots it is evident that in the carbonizing temperature range, 500° to 1,100° C., the composition-temperature relation for all carbonaceous materials can be represented by a straight line. This is true whether the composition is represented by the atomic hydrogen-carbon ratio or by the hydrogen content. The slope of this line probably is not too different from that of Lowry's line for cokes from bituminous coals. Therefore, the composition of the solid product above the decomposition temperature of the parent carbonaceous material depends essentially upon the carbonizing temperature.

A plot based on Blayden and co-workers' data (9-11) (Figure 3) shows that when a carbonaceous material is heated, little change in the crystallite diameter of the resulting chars occurs up to the decomposition temperature of the material. Above this temperature the relation between the crystallite diameter and the carbonizing temperature generally follows a common straight line for all cokes and chars from carbonaceous materials of widely different composition. This correlation is similar to that between composition of cokes and chars and carbonizing temperature shown in Figures 1 and 2.

Diamond (13) showed the same pattern in his plots for the relation between the mean layer size of cokes and chars from three bituminous coals and an anthracite and the carbonizing temperature up to 1,000° C., and in those for the relation between the mean bond length and the temperature up to 900° C. At a given carbonizing temperature the mean layer size of char from the anthracite was larger than the corresponding sizes for cokes and chars from the bituminous coals, but there was very little difference in layer size in cokes and chars from bituminous coals. A similar relation held between temperature and mean bond lengths of cokes and chars from these coals.

Thus, crystallite diameter and mean bond length of cokes and chars, particularly from bituminous coals, depend largely upon the carbonizing temperature between 500° and 1,000° C.

Finally, Franklin (14) found virtually the same density in the range 1,000° to 3,000° C. for cokes and chars prepared from different graphitizing carbonaceous materials at corresponding temperature, but discrepancies existed among those from nongraphitizing materials.

Method for Calculating Specific Volumes of Components of Carbonized Carbonaceous Materials

The foregoing facts indicate that mineral-matter-free cokes and chars prepared at the same temperature, in the range 500° to 1,000° C., and from carbonaceous materials of similar composition such as bituminous coals, may be treated univariantly for statistical purposes.

The composition and density of mineral matter in coals may be expected to differ, but such differences will be reduced in cokes and chars prepared at the same carbonizing temperature. Further, cokes from a well prepared sample of a carbonaceous material usually contain only a small fraction of mineral matter. Accordingly, the effect of the differences in the mineral-matter density upon the result of the calculated specific volume of the mineral-matter-free coke will be minor. In this work the assumption has been made that in the carbonizing temperature range between 500° and 1,000° C. the density of the mineral matter in cokes from different carbonaceous materials but prepared at the same carbonizing temperature is constant.

The foregoing discussion makes it evident that cokes prepared from coals at the same carbonizing temperature in the range 500° - 1,000° C. may be considered as a binary solid mixture, namely, a system composed of two pure solid components, the mineral matter and the carbonaceous matter.

According to the law of mixtures, the density of a mixture of two components can be calculated by the following relation:

$$D_m = (w_1 + w_2) / (v_1 + v_2) \dots \dots \dots (1)$$

where D_m represents the density of the mixture; w_1 and w_2 , the masses of the components; v_1 and v_2 , their respective volumes.

By definition,

$$D_1 = w_1 / v_1, \text{ or } v_1 = w_1 / D_1 \dots \dots \dots (2)$$

and,

$$D_2 = w_2 / v_2, \text{ or } v_2 = w_2 / D_2 \dots \dots \dots (3)$$

where D_1 and D_2 are densities of the components. If the masses of two components are expressed on a percentage basis, then

$$w_1 = 100 - w_2 \dots \dots \dots (4)$$

Substituting equations (2), (3), and (4) into equation (1), we obtain

$$D_1 = (100 - w_2) / (100/D_m - w_2/D_2) \dots \dots \dots (5)$$

In applying equation (5) to the system of cokes from carbonaceous materials, D_1 will represent the density of the carbonaceous matter or the mineral-matter-free coke; D_2 , the density of the mineral matter in the coke; D_m , the density of coke; w_2 , the mass percent of the mineral matter in the coke. A similar equation has been used for calculating the density of mineral-matter-free coal (12).

When equation (5) is solved for $1/D_m$, the following relation is obtained:

$$D_m^{-1} = D_1^{-1} + 0.01 (D_2^{-1} - D_1^{-1}) w_2 \dots \dots \dots (6)$$

Hence the reciprocal density, or specific volume, of coke varies linearly with its mineral-matter content. The y-intercept of the line of equation (6), obtained by extrapolating the mineral-matter content of coke to zero, is equal to the specific volume of mineral-matter-free coke.

Rigorous application of equation (6) can be made only when the amount of mineral matter in coke is known. Determination of mineral matter as such is difficult. However, data are available for the ash content of coke, determined by standard methods. We may consider the ash content to be proportional to the mineral-matter content,

$$w_2 = kA \quad (7)$$

where A is ash content and k a constant. Combining equations (6) and (7), and designating the specific volume of coke as V_m and that of mineral-matter-free coke as V_p , we obtain

$$V_m = V_p + 0.01 k (D_2^{-1} - D_1^{-1}) A \quad (8)$$

Since coke is assumed to be a binary solid system, D_2 and D_1 are constant for materials carbonized at the same temperature. As a result, the coefficient of A in equation (8) is a constant, K, and

$$V_m = V_p + K A \quad (9)$$

This equation assumes a linear relation between specific volume and ash content of cokes prepared from different carbonaceous materials at the same temperature. The specific volume of the mineral-matter-free coke, $1/D_1$, can be determined from the intercept, the specific volume of the mineral matter in the coke, $1/D_2$, can be calculated from K in equation (9) if a value is known or assumed for k in equation (7).

Data on Cokes from Bituminous Coals

Data from Bureau of Mines-American Gas Association (BM-AGA) carbonization tests on 41 coals have been used for this study. These coals include the following numbers in the Bureau of Mines survey on the carbonizing properties of American coals: 10, 13-23, 26, 27, 31, 53, 54, 57-59, 62-64, 66-68, 71, 72, 75, 76, 81, 82, 85-91, 93, and 94. All are coking except 85.^{4/} Their volatile-matter content on a dry, ash-free basis ranged from 16.3 to 46.7 percent, covering almost the whole range of bituminous coals. Their oxygen contents on the same basis ranged from 2.1 to 17 percent, largely below 8, and sulfur contents from 0.5 to 2.9 percent, largely below 1. Their atomic hydrogen-carbon ratio ranged from 0.571 to 0.928.

All 41 coals were carbonized at 600° to 1,000° C. at 100° C. intervals, but only 37 (all except 90, 91, 93 and 94) at 500° C. Carbonizations were carried out in the 13-inch retort, and in a few instances at 800°, 900°, and 1,000° C. in the 18-inch retort. Almost all the data are averages of duplicate tests.

^{4/} Char from this coal will be referred to as coke in this paper.

Variance analysis on data of several coals carbonized at 800°, 900° and 1,000° C. in both retorts shows that at 5 percent significance level size of the retort has no effect on density or on the hydrogen and the carbon contents of cokes. But the effect of the parent coal upon the density of the resulting coke appears significant at the same significance level. This effect apparently is largely because of the difference in the mineral-matter content among coals, although in a higher carbonizing temperature range (1,000° - 3,000° C.) it has been found (14) that the density of cokes and chars depends not only upon the carbonizing temperature but also on whether the material carbonized is graphitizing or nongraphitizing. Even if such an effect of the parent material exists between 500° and 1,000° C., it is largely eliminated in this study since almost all coals were carbonized at each temperature.

Specific volumes of cokes at each carbonizing temperature have been correlated with ash contents on the dry coke basis, and the least-squares method has been used to fit a linear regression line. As mentioned in the preceding section, the y-intercept of this line represents the specific volume of the mineral-matter-free coke at the same temperature. Both y-intercepts and slopes of least-squares lines for 500° to 1,000° C. cokes are shown in Table 1. It should be emphasized that until more general application is demonstrated this specific volume of the mineral-matter-free coke thus obtained can only be considered as an average value for the 41 coals studied. Table 1 also includes correlation coefficients, standard deviations of estimate, and standard deviations of y-intercepts of the regression lines.

TABLE 1.- Results of Correlation Between Specific Volumes and Dry Ash Contents of Cokes from Bituminous Coals

$$V_m = V_p + KA$$

Carbon- izing tempera- ture, °C.	Number of samples	V_p (y-intercept)	K (slope)	Correlation coefficient	Standard deviation of V_m	Standard deviation of V_p
500	37	0.707	-0.00350	0.879	0.0064	0.0025
600	41	.650	- .00167	.571	.0082	.0032
700	41	.587	- .00138	.545	.0076	.0027
800	41	.554	- .00138	.606	.0067	.0026
900	41	.545	- .00180	.718	.0063	.0025
1,000	41	.538	- .00112	.392	.0096	.0037

The average specific volumes of both actual coke and mineral-matter-free coke decrease in a similar manner with the carbonizing temperature in the range 500° to 1,000° C. (Figure 4 and Table 2). For the mineral-matter-free coke, the relation is linear in the range 500° to 700° C., and again linear, but with different slope and intercept in the range 800° to 1,000° C. In Figure 4, these functions are represented by dotted lines which intersect at about 700° C. Below 700° C. the dotted line coincides with the solid curve.

TABLE 2.- Average Values of Specific Volumes and Atomic Hydrogen-, Oxygen-, and Nitrogen-Carbon Ratios of Bituminous Cokes.

Carbon-izing temperature, °C.	Num-ber of sam-ples	Ash con-tent on dry basis, %	Avg. spec-ific vol-ume of coke	Avg. spec-ific vol. of mineral-matter-free coke	Composition of coke *						Skeleton hydrocarbon of mineral-matter-free coke		
					Atomic H/C		Atomic O/C		Atomic N/C				
					Avg. value	Stand-ard devia-tion	Stand-ard devia-tion	Avg. value	Stand-ard devia-tion	Avg. value	Stand-ard devia-tion	Spec-ific vol-ume	Atomic H/C
500	37	7.10	0.682	0.707	0.445	0.014	0.032	0.008	0.018	0.003	0.753	0.500	0.025
600	41	7.51	.637	.650	.326	.015	.020	.004	.016	.002	.683	.368	.017
700	41	7.87	.576	.587	.206	.013	.012	.004	.015	.002	.612	.239	.013
800	41	8.00	.543	.554	.140	.014	.007	.004	.014	.002	.574	.165	.015
900	41	8.08	.531	.545	.088	.012	.003	.002	.013	.002	.561	.106	.014
1000	41	8.08	.528	.538	.057	.009	.002	.001	.011	.002	.550	.071	.011

* On dry, sulfur- and ash-free basis.

The change of slope at about 700° C., as shown in Figure 4, indicates this temperature to be significant in the process of carbonization. This is supported by characteristic changes in other physical properties of cokes prepared at about the same temperature. Maximum moisture absorption (15) and carbon-dioxide adsorption (16) have been reported for cokes prepared at about 700° C. A sharp increase in electrical conductivity (16-19) and a decrease in magnetic susceptibility (20) also have been determined to occur for cokes prepared at about the same temperature. Furthermore, widely different carbonaceous materials gave off a maximum amount of hydrogen during carbonization between 700° and 800° C. (5), (21-23).

Figure 5 shows that the atomic hydrogen- and oxygen-carbon ratios for cokes carbonized at 500° to 1,000° C. may also be represented by two straight lines which intersect at about 700° C. The slope of these lines is greater at lower than at higher temperatures. The atomic nitrogen-carbon ratio is linear throughout the whole temperature range. These facts, together with those mentioned in the last two paragraphs, indicate two stages of reactions in the process of carbonization. In the range of 500° to 700° C., chemical reactions occur which may result in disruption of the carbon skeleton of the coal molecule and rearrangement of the newly formed radicals and/or molecules. Above this temperature range, the principal reaction may be condensation of the radicals and/or molecules from the first stage, perhaps accompanied by dehydrogenation. Both condensation and dehydrogenation result in elimination of hydrogen, the major gaseous product above 700° to 800° C.

The specific volume of mineral-matter-free coke prepared between 500° and 1,000° C. varies linearly with the atomic hydrogen- and oxygen-carbon ratios as well as with the carbon content of the coke. The least-squares line for the atomic hydrogen-carbon ratio of mineral-matter-free coke lies above that for crystalline polycyclic aromatic compounds (24), as shown in Figure 6. From the standard deviation of estimate of the latter line, data for the former line are not expected to overlap those for the latter. Further, all coke data fall above the crystalline polycyclic aromatics line. These facts indicate an imperfect crystalline structure of cokes, as was also found to be true for high rank coals (24).

The line for mineral-matter-free coke approaches that for crystalline polycyclic-aromatics more closely with increasing atomic hydrogen-carbon ratios or decreasing carbonizing temperatures. This is evidently largely due to the occurrence of oxygen and nitrogen in coke. However, one can correct for the presence of oxygen and nitrogen. This hypothetical hydrocarbon has been designated as the skeleton hydrocarbon of mineral-matter-free coke.

Occurrence of oxygen and nitrogen in coke indicates that their linkages, possibly all with carbon atoms, in the coke molecule must be strong. Thus, it is assumed that all the oxygen and nitrogen in coke exist in heterocyclic structures. Using Traube's values of atomic volumes (25), one finds that displacement of each oxygen atom in the heterocyclic compound by one CH₂ group results in an increase of 10.6 cc. per gram-molecular volume, and displacement of each nitrogen atom by one CH group, in an increase of 11.5 cc. If O_H and N_H represent the numbers of oxygen and nitrogen atoms, respectively, in the mineral-matter-free coke, the heterocyclic compound, the total increase in the gram-molecular volume due to displacement is 10.6 O_H + 11.5 N_H. Similarly, a decrease in gram-molecular weight

due to change of a heterocyclic compound into a corresponding carbocyclic one is $1.974 O_H + 0.990 N_H$. In other words,

$$V_C = V_H + 10.6 O_H + 11.5 N_H \quad (10)$$

$$W_C = W_H - 1.974 O_H - 0.990 N_H \quad (11)$$

where V_H and W_H represent gram-molecular volume and gram-molecular weight of the heterocyclic compound, and V_C and W_C those of the carbocyclic compound.

If S_H be the specific volume of the heterocyclic coke molecule and S_C that of the corresponding carbocyclic compound, then

$$S_C = V_C / W_C \quad (12)$$

Substituting equations (10) and (11) into equation (12) and dividing numerator and the denominator by CH , the number of carbon atoms in the heterocyclic coke molecule, we obtain

$$S_C = (V_H / CH + 10.6 O_H / CH + 11.5 N_H / CH) / (W_H / CH - 1.974 O_H / CH - 0.990 N_H / CH).$$

$$\text{Since } V_H / CH = V_H / W_H \times W_H / CH = S_H W_H / CH \quad (13)$$

therefore,

$$S_C = (S_H W_H / CH + 10.6 O_H / CH + 11.5 N_H / CH) / (W_H / CH - 1.974 O_H / CH - 0.990 N_H / CH) \quad (14)$$

If C, O, and N represent, respectively, the number of atoms of carbon, oxygen, and nitrogen per 100 grams of the heterocyclic compound, which can be calculated from ultimate analysis data, then $W_H / CH = 100 / C$; $O_H / CH = O / C$; $N_H / CH = N / C$.

Therefore, from equation (14),

$$S_C = (S_H 100 / C + 10.6 O / C + 11.5 N / C) / (100 / C - 1.974 O / C - 0.990 N / C) \quad (15)$$

Using equation (15) and average values from Table 2 for atomic ratios and specific volumes of the mineral-matter-free cokes at different carbonizing temperatures, the specific volumes of the skeleton hydrocarbons of the cokes are calculated. The result are shown in Table 2, and the least-squares line of the calculated values is plotted in Figure 6. The line is almost parallel to the crystalline polycyclic aromatics line. This fact is in accord with the earlier statement that the occurrence of oxygen and nitrogen in the coke is largely responsible for the mineral-matter-free coke line lying closer to the polycyclic aromatics line in the region of high atomic hydrogen-carbon ratios. Also, correction for nitrogen and oxygen content shows that the significance of the data for mineral-matter-free cokes is the same, regardless of temperature, as an indication of a disordered crystalline structure in cokes.

Comparison of average values of atomic oxygen-carbon ratios with their standard deviations in Table 2 shows that the experimental error is large compared with

the oxygen content because it is obtained by the difference between 100 and the sum of percentages of ash, sulfur, carbon, hydrogen, and nitrogen in the ultimate analysis. However, the effect of this error upon the calculated specific volume of the skeleton hydrocarbon is negligible.

The difference between the lines for the mineral-matter-free coke and the skeleton hydrocarbon, as shown in Figure 6, decreases with decreasing atomic hydrogen-carbon ratio of the coke. Such difference should reduce to zero at zero value of the atomic hydrogen-carbon ratio of the coke. This agrees with the fact that the y-intercepts of the equations for these lines are almost identical. This point of intersection may be considered as the specific volume of a hypothetical, pure carbon. However, until data for higher temperatures are available, the relationship between the specific volume and the atomic hydrogen-carbon ratio, whether of mineral-matter-free coke or its skeleton hydrocarbon, must be restricted to the carbonizing temperature or the atomic hydrogen-carbon ratio range studied.

Table 3 shows the least-squares equations and their correlation coefficients for the lines in Figure 6 for crystalline polycyclic aromatic hydrocarbon, mineral-matter-free coke, and skeleton hydrocarbon.

TABLE 3. - Least-Squares Equations for the Relationship Between Specific Volume and Atomic Hydrogen-Carbon Ratio of Different Classes of Substance

Class of substance	Equation	Correlation coefficient
Crystalline polycyclic aromatic hydrocarbon *	Sp. vol. = $0.457 + 0.508 \text{ H/C}$	0.978
Mineral-matter-free bituminous coke	Sp. vol. = $0.502 + 0.450 \text{ H/C}$.993
Skeleton hydrocarbon of mineral-matter-free bituminous coke	Sp. vol. = $0.506 + 0.483 \text{ H/C}$.994

* From bibliographic reference 24.

It has been mentioned that the density of the mineral matter in coke can be calculated from equation (8) if the value of k is known. For approximation, k may be assumed equal to unity, considering the difference between the determined ash content and the mineral-matter content in coke to be negligible. The average calculated density of ash in cokes prepared between 500° and 1,000° C. varies between 2.1 and 2.8, with 2.4 as an average value. Density determinations have been made of the ash of Hernshaw Bed coal; for the whole coal, the density is 2.71; for the bright band, 2.67; and for the dull band, 3.03. A value of 2.7 for coal ash has been reported in the literature (12).

CONCLUSIONS

It has been shown that the composition of the solid carbonization product, whether judged by the atomic hydrogen-carbon ratio or the hydrogen content of the product, depends largely upon the carbonizing temperature in the range from the decomposition temperature of the parent material up to 1,100° C.

The decomposition temperature of carbonaceous materials varies with their composition. Below this temperature, little change occurs in the composition of the solid carbonization product, but above it the composition-temperature relation of the product follows a common straight line for cokes and chars from widely different carbonaceous materials.

Changes of crystallite diameters and the mean bond lengths of cokes with the carbonizing temperature up to about 1,000° C. generally follow the same trend as that for the composition.

A linear relation has been shown between specific volume and ash content of cokes. The intercept of such a line corresponds to the average specific volume of mineral-matter-free coke, and the slope is related to the specific volume of the mineral matter in coke.

A temperature of about 700° C. has been found to be significant in the carbonization process. This is supported by the relations of carbonizing temperature to specific volume of mineral-matter-free coke and to its average atomic hydrogen- and oxygen-carbon ratios. These relations indicate--as has other experimental evidence--two stages of reactions. Chemical reactions up to about 700° C. may result in disruption of the carbon skeleton of the coal molecule and rearrangement of newly formed radicals and/or molecules, while above this temperature the principal reaction may be condensation of the radicals and/or molecules from the first stage, perhaps accompanied by dehydrogenation.

The specific volumes of mineral-matter-free cokes prepared in the temperature range from 500° to 1,000° C. are greater than those of the crystalline polycyclic aromatic hydrocarbons having the same atomic hydrogen-carbon ratios, indicating a disordered structure of the cokes. The same conclusion can be drawn from a comparison of specific volumes of the hypothetical aromatic hydrocarbons corresponding to oxygen-, nitrogen, and mineral-matter-free cokes with those of the polycyclic aromatic hydrocarbons. An equation has been derived for calculating the specific volume of the hypothetical hydrocarbons from that of their parent mineral-matter-free cokes.

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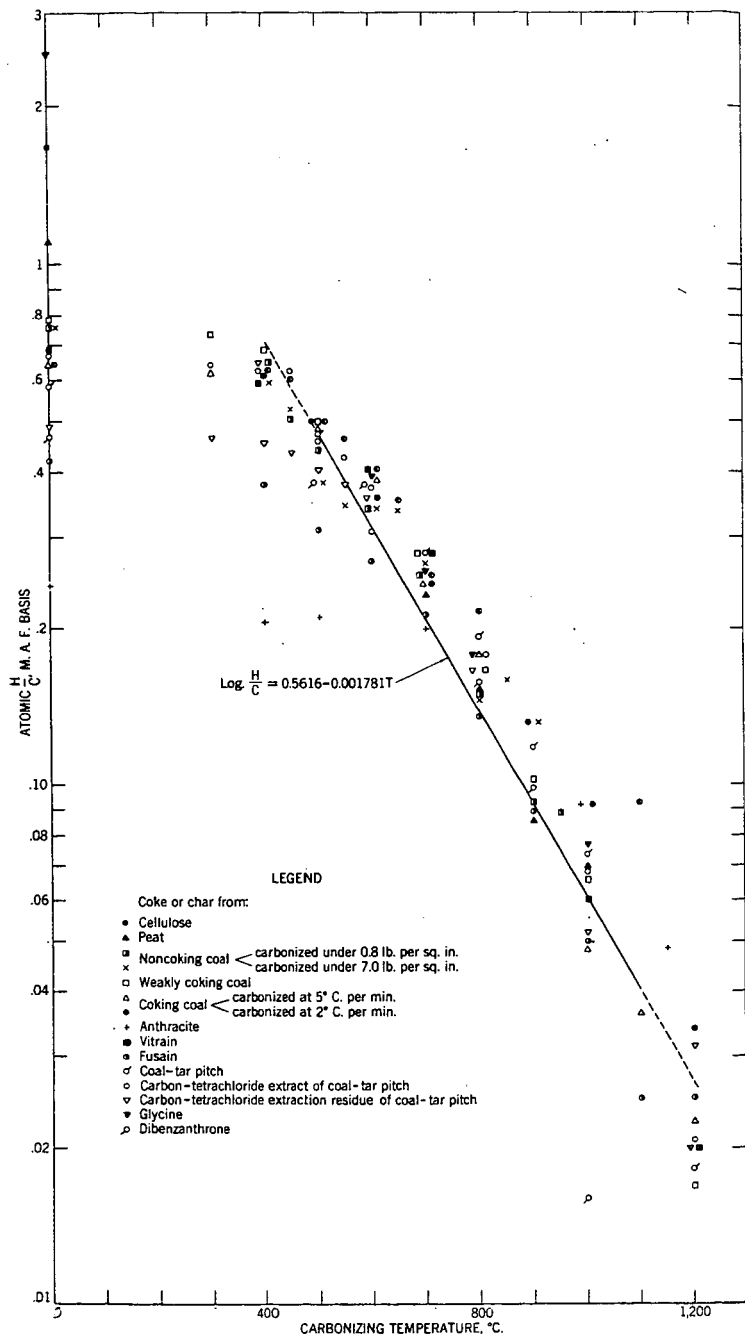


Figure 1. - Relationship between atomic hydrogen-carbon ratio and carbonizing temperature.

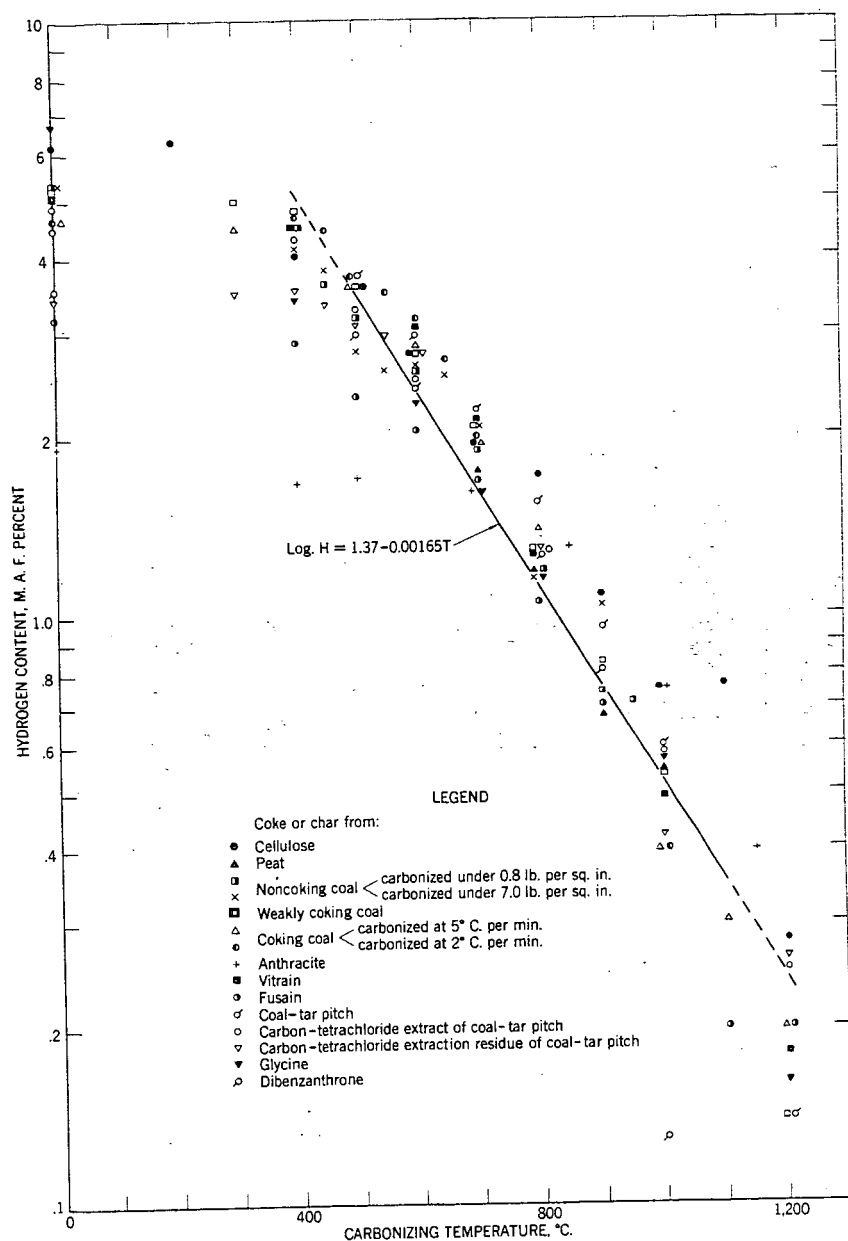


Figure 2. - Relationship between hydrogen content and carbonizing temperature.

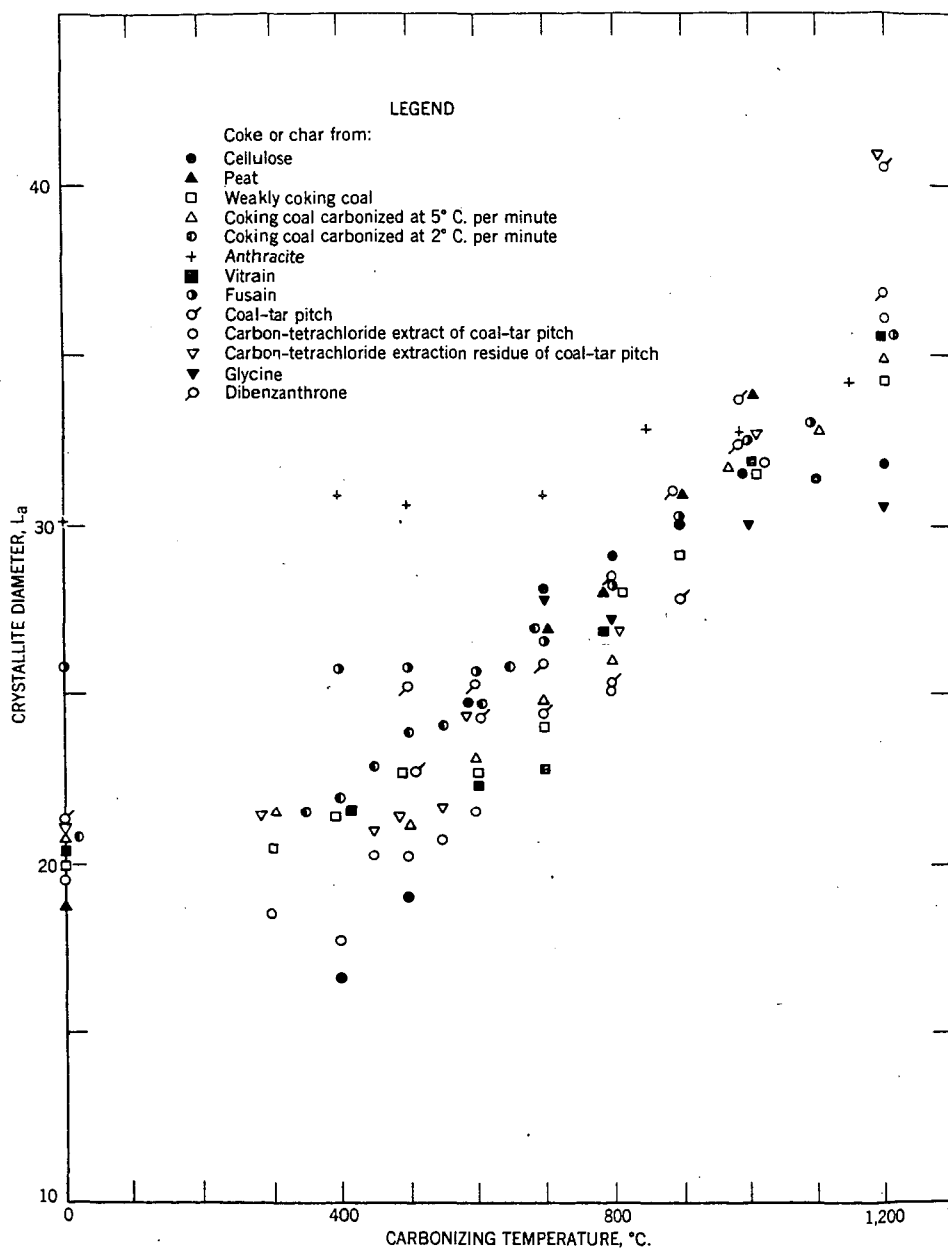


Figure 3. - Relationship between crystallite diameter and carbonizing temperature.

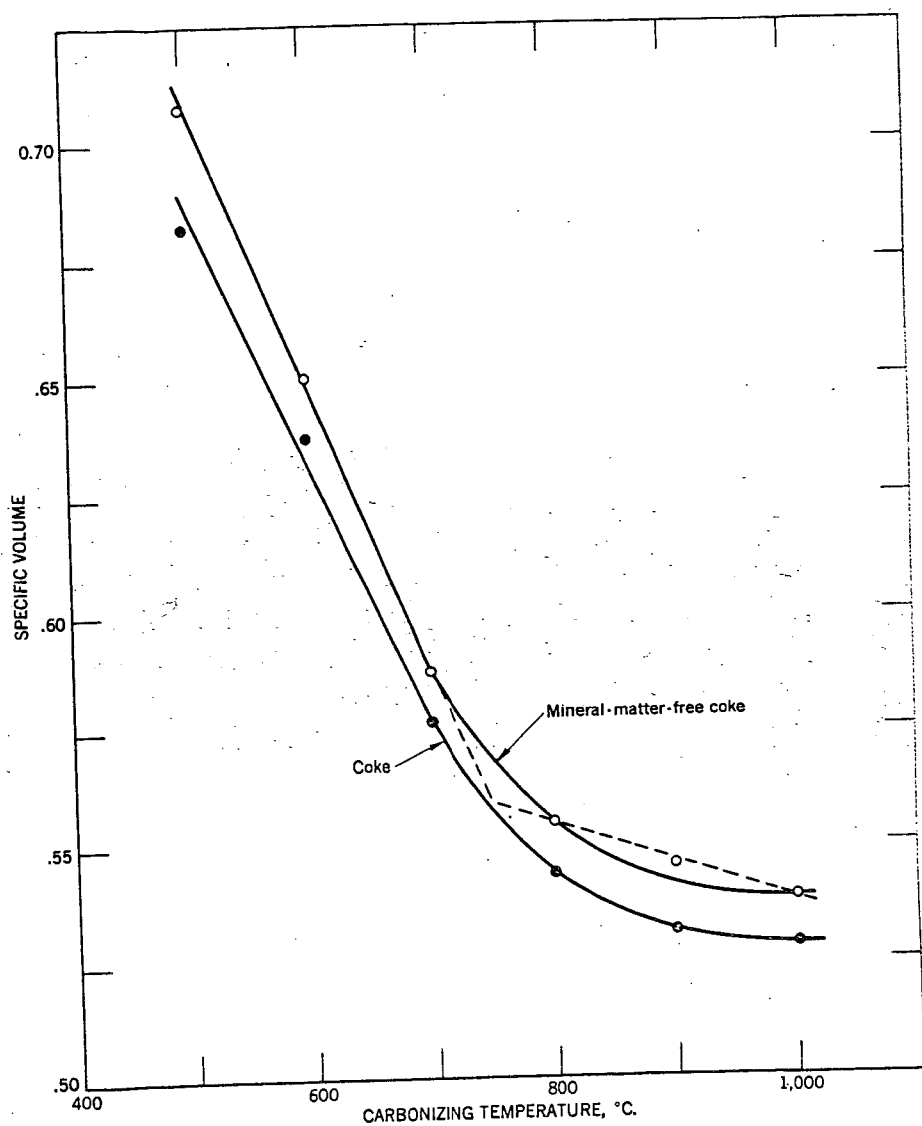


Figure 4. - Relationship between specific volume of coke and carbonizing temperature.

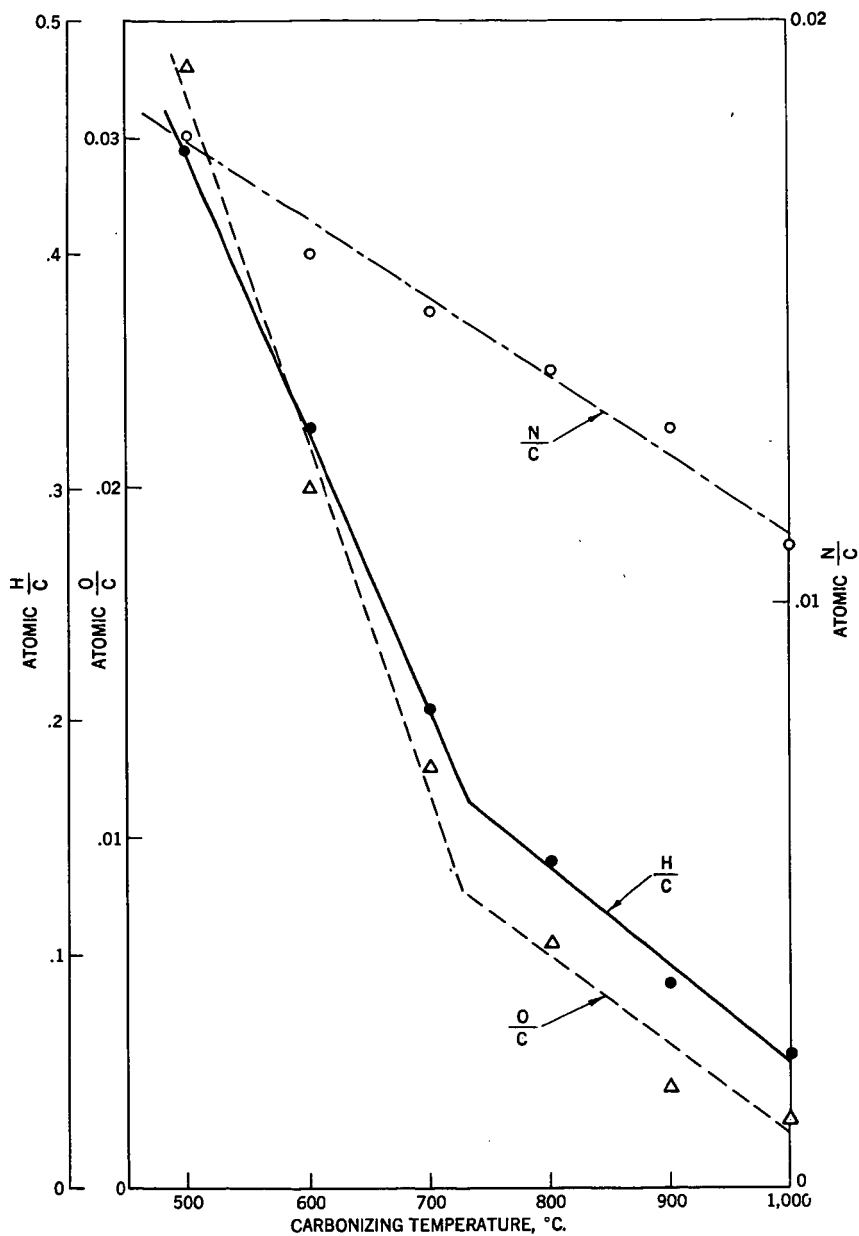


Figure 5. - Relationship between average composition of coke (moisture-, sulfur-, and ash-free basis) and carbonizing temperature.

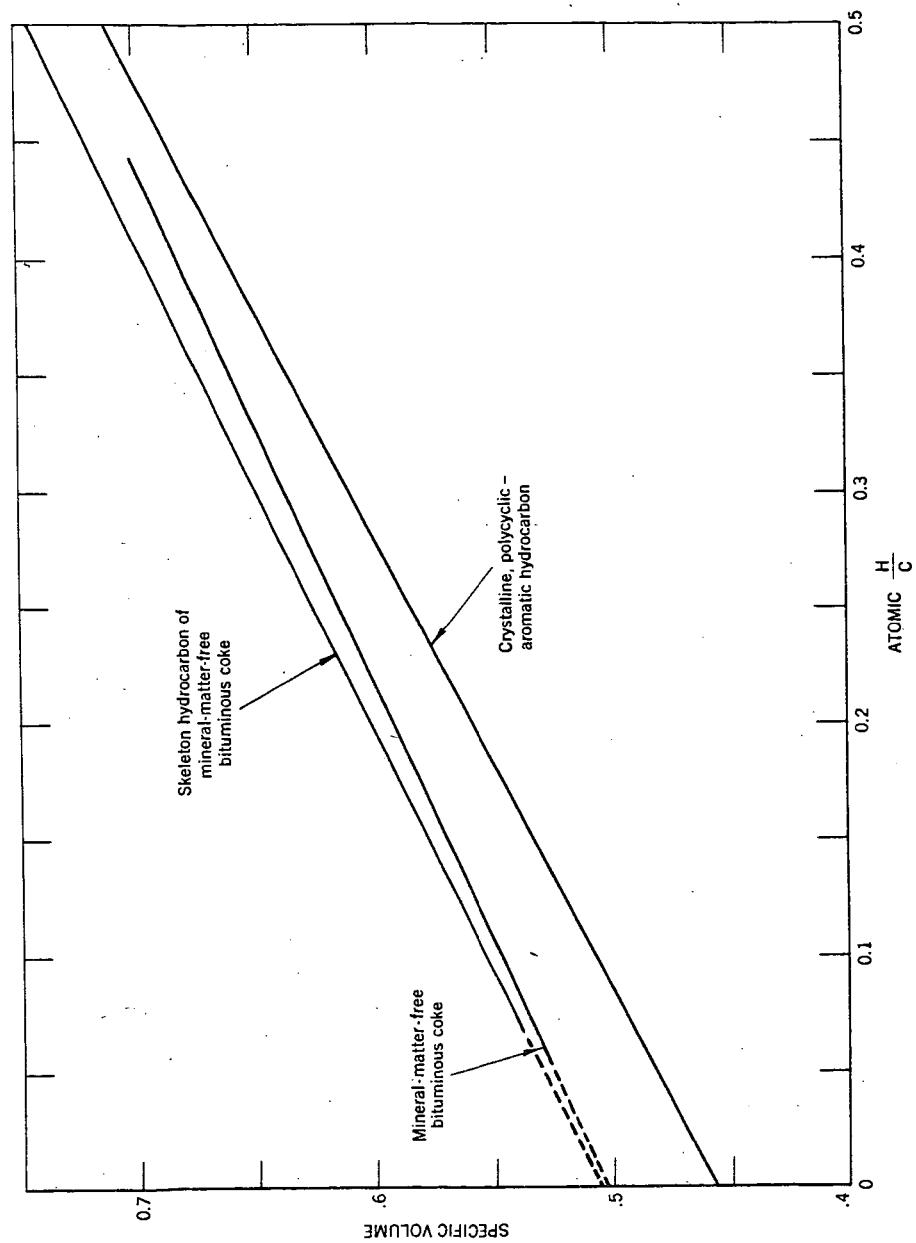


Figure 6. - Relationship between specific volume and atomic hydrogen-carbon ratio of different classes of substance.